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A Modified Hydrated Ferric Oxyhydroxide
Impregnated Filter Paper Technique:
Sorption Of Copper, Zinc and Nickel
From Solution

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4 A MODIFIED HYDRATED FERRIC OXYHYDROXIDE-IMPREGNATED

5 FILTER PAPER TECHNIQUE:

6 SORPTION OF COPPER, ZINC AND NICKEL FROM SOLUTION
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1 A MODIFIED HYDRATED FERRIC OXYHYDROXIDE-IMPREGNATED FILTER PAPER

2 TECHNIQUE: SORPTION OF COPPER, ZINC AND NICKEL FROM SOLUTION

3
4 ABSTRACT

5 Ferrihydrite, poorly crystalline to amorphous hydrated ferric
6 oxyhydroxide (HFO), plays an important role in the control of trace metal
7 concentrations in soil solutions and natural waters. The objectives of
8 this study were to test sorption of Cu, Zn, and Ni by a modified HFO-
9 impregnated filter paper technique, and (1) determine the effects of pH on
10 sorption, and (2) its potential use in differentiating sorption processes
11 from cation precipitation in the bulk solution. Sorption of metal cations
12 from solution (0.01 M CaCl_2) was carried out at pH levels of 4 to 11 and
13 initial concentrations from 10^{-6} to 10^{-3} M. Metal cation sorption was
14 modeled using MINTEQA2 and the diffuse-layer (surface complexation) model.
15 Metal hydroxide solubilities in the absence of a sorbent phase, were also
16 modeled by MINTEQA2. By providing two *independent* measurements, HFO-
17 strips were not only successful in differentiating bulk solution
18 precipitation from surface complexation, but described sorption at high pH
19 values, where current techniques are not applicable. Sorption at pH
20 levels higher than the initial s-shaped pH-edges is controlled by the
21 solubility of the metal hydroxides. Therefore, metal sorption occurs in
22 a wide range of pH. The modified HFO-impregnated filter paper technique
23 is potentially suitable for the quantitative determination of multielement
24 release from soils and other natural aqueous systems.

1 Hydrous oxides of iron play an important role in the control of
2 trace metal concentrations in soil solutions and natural waters (Jenne,
3 1968; Singh and Subramanian, 1984). Ferrihydrites, poorly crystalline to
4 amorphous hydrated ferric oxyhydroxides (HFO), can sorb a host of chemical
5 species and are some of the dominant sorbents in natural systems (Dzombak
6 & Morel, 1990). Numerous metal cation sorption studies onto ferrihydrite
7 in natural environments (Johnson, 1986; Amacher et al., 1993) as well as
8 under laboratory conditions (Kinniburgh et al., 1976; Benjamin, 1983) are
9 found in the literature.

10 Kurbatov and co-workers (1951) were the first to recognize the pH
11 dependence of metal adsorption onto hydrous ferric oxides. Cation
12 sorption increases with increasing pH, and the fraction remaining in
13 solution goes from one to zero in a relatively narrow pH range,
14 particularly for strongly hydrolyzable cations (Kinniburgh and Jackson,
15 1981). According to Dzombak and Morel (1990), as adsorption sites become
16 saturated, a plateau is reached at a level below 100 percent sorption.
17 But the pH at which site saturation occurs may be obscured due to
18 hydroxide precipitation, in solution or at the surface, prior to bulk
19 solution precipitation (Benjamin, 1983; Farley et al., 1985).

20 In an accompanying paper (Buselli and Amacher, 1994) we evaluated
21 sorption of arsenate and phosphate from solution onto a modified HFO-
22 impregnated filter paper technique based on the one proposed by Van der
23 Zee et al. (1987). Potentially, the technique could be used for the
24 evaluation of multielement release from soils, sediments, and natural
25 waters. Furthermore, it could also prove valuable in elucidating

1 processes at solid/liquid interfaces due to some advantages over current
2 methodology used in the study of solute sorption onto hydrous oxides
3 (Buselli and Amacher, 1994).

4 Accordingly, the objectives of this study were to test transition
5 metal sorption by the modified HFO-impregnated filter paper technique,
6 determine the effects of pH on its sorption properties, and its usefulness
7 in differentiating sorption processes from bulk solution precipitation.
8 In this paper we summarize the results of sorption studies with copper,
9 zinc, and nickel.

11 MATERIALS AND METHODS

13 Preparation of the HFO-impregnated strips

14 The strips were prepared according to the method described
15 previously (Buselli and Amacher, 1994). Two treatments in 2.7 M NH_4OH
16 followed by thorough washing of the HFO-strips in deionized water were
17 used for all experiments.

18 Sorption Experiments

19 Sorption experiments were carried out in duplicate batch systems.
20 HFO-strips were prepared fresh daily, placed in 250-ml polycarbonate jars
21 and then 80 ml of solution containing the desired metal cation in 0.01 M
22 CaCl_2 were added. For all studies, chloride salts of Cu^{2+} , Zn^{2+} and Ni^{2+}
23 were used. The jars were shaken at 150 rpm in an orbital shaker at $25^\circ \pm$
24 1°C for a predetermined amount of time. After shaking, the strips were
25 removed from the jars, immersed in a beaker filled with deionized water

1 and washed thoroughly. They were then removed from the plastic frames,
2 air dried, and placed in 50-ml centrifuge tubes. Extraction of Fe and the
3 sorbed species was done with 25-ml of 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 0.25 M HCl (Chao
4 and Zhou, 1983) for 15 min at 180 rpm on a reciprocating shaker.
5 Concentrations of Ca, Fe and the metal cation of interest (Cu, Zn or Ni)
6 left in solution (dissolved) and in the extractions (sorbed) were
7 determined by means of ICAPES. The pH was determined, after removal of
8 the strip, with an Orion AE940 Expandable IonAnalyzer with a Ross
9 combination electrode. The electrode was considered equilibrated when the
10 rate of change was less than 0.01 pH units in a 2-min period (Anderson and
11 Malotky, 1979).

12 *Sorption Envelopes* - Preliminary experiments were carried out to
13 determine the appropriate acid (0.5 M HCl) and base (0.5 M NaOH) additions
14 necessary to obtain the desired range of final pH. All additions were
15 less than 2% of the total solution volume. Initial concentrations were
16 determined to be 92.8×10^{-6} M Cu, 92.5×10^{-6} M Zn and 97.1×10^{-6} M Ni.
17 After addition of acid or base the strips were placed in the jars and they
18 were shaken for 16 h.

19 *Sorption Capacity* - Strips were placed in 10, 50, 100, 200, 300, 400, 500,
20 600, 700, 800, 900, and 1000 $\times 10^{-6}$ M solutions of each metal cation. The
21 solutions were shaken for 16 h.

22 Predicted sorption by chemical modeling

23 *MINTEQA2/PRODEFA2 v 3.0* - MINTEQA2 is a chemical equilibrium speciation
24 model for dilute aqueous systems, while the interactive program PRODEFA2
25 creates input files for MINTEQA2 (Allison et al., 1990). MINTEQA2 is

capable of computing equilibria among dissolved, solid (precipitated), and gas phases. Adsorbed phases, using several models, can be predicted by manually inputting adsorption constants or attaching auxiliary databases. *FEO-DLM.DBS* - *FEO-DLM.DBS* is an auxiliary database file containing surface reactions and their respective intrinsic constants for the diffuse-layer model (DLM) based on the extensive data compilation of Dzombak and Morel (1990) for hydrous ferric oxides. The parameters used to model metal cation adsorption with MINTEQA2 are listed in Table 1 and further details can be found elsewhere (Buselli and Amacher, 1994). Table 2 lists the surface reactions attached to MINTEQA2 from *FEO-DLM.DBS*.

RESULTS AND DISCUSSION

Sorption envelopes for the three divalent metal cations are shown in Figure 1. Copper adsorption (Fig. 1a) increased rapidly from pH 4 to 6. The maximum observed adsorption was 82.5 % at pH 5.88. From pH ≥ 6 to 7.5 there was a sharp decrease in % Cu adsorbed and adsorption from pH 7.5 to > 10 remained relatively constant at 15 to 18 %. Decrease in copper adsorption with pH has been previously reported for illite (O'Connor and Kester, 1975) and modeled for silica (Schindler, 1981). According to Schindler (1981) the pH range could be separated in two parts: (1) pH range of increasing adsorption, and (2) pH range of increasing desorption. Desorption of copper was attributed to the formation of anionic hydroxo complexes (O'Connor and Kester, 1975; Baes and Mesmer, 1976; Schindler, 1981) at pH values > 12 . Under our experimental conditions, predicted

1 concentrations even at pH 7.5 (higher end of the "pH desorption range")
2 were in the order of 10^{-13} M $\text{Cu}(\text{OH})_3^-$ and 10^{-18} M $\text{Cu}(\text{OH})_4^{2-}$, suggesting no
3 major influence in the sharp reduction in sorption.

4 Zinc sorption versus pH (Fig. 1b) followed a similar pattern.
5 Although desorption occurred at pH values from 6.5 to 9, it reached a
6 minimum of about 50% removal from solution after which increased sorption
7 with increasing pH resumed. On the other hand, nickel sorption (Fig. 1c)
8 reached a maximum at around pH 6.8, decreased steadily with increasing pH,
9 and practically no sorption occurred at pH > 8.

10 Calculated sorption values obtained from metal removal from solution
11 (see Fig. 1) agreed reasonably well with the HFO-strip sorption data from
12 low pH up to pH values where sorption maxima occurred. Furthermore,
13 initial adsorption with increasing pH (pH edges) for Cu (Fig. 1a), Zn
14 (Fig. 1b), and Ni (Fig. 1c) followed a selectivity sequence widely
15 reported for a variety of sorbents. The relative order of sorption $\text{Cu} >$
16 $\text{Zn} > \text{Ni}$ has been reported for oxides of aluminum (Kinniburgh et al.,
17 1976), iron (Kinniburgh et al., 1976; Venkataramani et al., 1978;
18 McKenzie, 1980), manganese (Kozawa, 1959; McKenzie, 1972, 1980; Murray,
19 1975), and tin (Donaldson and Fuller, 1968) also for humic acids (Rashid,
20 1974; Kerndorff and Schnitzer, 1980) and a variety of soils (Andersson,
21 1977; Biddappa et al., 1981; Harter, 1983; Yamamoto, 1984).

22 On the other hand, at higher pH, calculated sorption failed to
23 describe metal removal by the HFO-strips and yielded typical pH edge s-
24 shaped curves plateauing at 100 percent sorption (Fig. 1). We believe
25 metal hydroxide precipitation can account for the sorption behavior at

1 high pH under these experimental conditions. For example, copper
2 concentrations used by O'Connor and Kester (1975) and Schindler (1981)
3 were in the order of 10^{-6} - 10^{-7} M and at those concentrations, formation of
4 $\text{Cu}(\text{OH})_2(\text{s})$ is unlikely (Baes & Mesmer, 1976). On the other hand, at higher
5 Cu concentrations ($\approx 10^{-4}$ M), MINTEQA2 predicts formation of $\text{Cu}(\text{OH})_2(\text{s})$
6 at pH > 6.5. As shown in Figure 2a, dissolved Cu decreases from 100 % at
7 pH 6.5 to 20 % at pH 7.0 (solubility constants for the metal hydroxides
8 are shown in Table 3).

9 Metal recovery, as calculated from two *independent* observations
10 (dissolved and adsorbed), follows predicted metal removal by cation
11 precipitation (with no sorbent phase present) reasonably well (Figure 2).
12 The data suggest that at low pH, metals are present either as dissolved or
13 adsorbed phases. Increasing pH, to values at which metal hydroxide
14 precipitation occurs, removes metals from solution to levels below
15 analytical detection limits and metals are bound in either adsorbed or
16 precipitated phases.

17 The fact that sorption processes occur at lower pH than metal
18 hydroxide precipitation in the bulk solution is well documented (e.g.,
19 Benjamin, 1983). Even so, at high metal concentrations, as sites become
20 saturated with increasing pH, this distinction becomes less clear (e.g.,
21 Tewari and Lee, 1975). Furthermore, separation of the sorption process
22 into adsorption and surface precipitation by measurement of the chemical
23 composition of an aqueous solution suffers from severe limitations
24 (Sposito, 1986).

25 Since metal recovery in experiments carried at pH < 6.5 was greater

1 than 96% for all three metal cations (see Table 4), losses in recovery at
2 higher pH can only be attributed to precipitation in the bulk solution and
3 onto plasticware surfaces, or formation of a loose surface precipitate
4 that is easily removed during the washing procedure. The experimental
5 shaking speeds are at least as vigorous as the washing step, therefore,
6 removal of a loosely held precipitate will probably occur during shaking.

7 In cobalt sorption studies on TiO_2 and SiO_2 , charge reversals in
8 electrophoretic mobility have been explained in terms of precipitation of
9 hydrolysis products on the solid surfaces at pH values lower than the ones
10 needed for bulk solution precipitation (James and Healy, 1972). Similar
11 reversals have been reported for alkaline-earth metals under conditions in
12 which hydrolyzed species were in the 10^{-6} to 10^{-8} M range and certainly not
13 a factor in the reversal of the zeta potential of TiO_2 (Fuerstenau et al.,
14 1981). More recent studies (Schenck et al., 1983) of cobalt sorption on
15 goethite at concentrations in the range 10^{-1} to 10^{-2} M, using
16 electrophoretic mobility and surface analysis by means of X-ray
17 photoelectron spectroscopy, seem to corroborate the findings of James and
18 Healy (1972), although much higher Co concentrations were used.

19 According to Sposito (1983) coprecipitation, a common phenomenon in
20 soil solutions and other natural water systems, can include formation of
21 a solid solution, adsorption, and inclusion. Although no structural
22 models have been presented, formation of a solid-solution has been
23 proposed as a sorption mechanism for phosphorus in soils (Blanchar and
24 Stearman, 1985), alumina (Miller et al., 1986), and ferrihydrite (Fox,
25 1989, 1990). Recently, Waychunas et al. (1993) and Fuller et al. (1993)

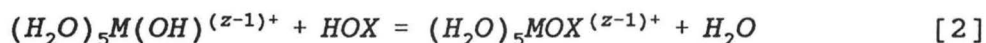
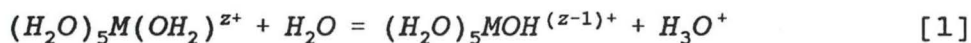
1 have reported that ferrihydrite coprecipitated with arsenate and post-
2 synthesis sorption of arsenate onto ferrihydrite yielded only surface
3 coordinated (adsorbed) As species as determined by extended X-ray
4 absorption fine structure spectroscopy (EXAFS). They also suggest that
5 due to the structure of ferrihydrite, formation of a solid solution with
6 arsenate or even phosphate is unlikely.

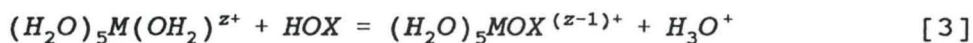
7 Since post-synthesis sorption experiments were carried out and no
8 dissolved Fe was detected in solution, coprecipitation phenomena can in
9 all likelihood, be ruled out. Although it can not be inferred directly
10 from the experimental data, adsorption seems to be the dominant mechanism
11 for dissolved metal removal by the HFO-strips. If surface precipitation
12 was occurring at pH levels lower than those needed for bulk solution
13 precipitation (Fig. 1), an increase in pH will induce additional
14 precipitation and reduced sorption by the strips will be unlikely.

15 Sorption of calcium from metal sorption envelope experiments (Fig.
16 1) is shown in Figure 3. Although Ca sorption was less than 5 % of total,
17 sorption maxima were predicted reasonably well by MINTEQA2/DLM. As
18 reported earlier (Buselli and Amacher, 1994), experimentally obtained Ca
19 sorption occurred at lower pH values than those predicted with the
20 diffuse-layer model. In a study of the effects of calcium on zinc
21 adsorption onto HFO, Dempsey and Singer (1980) found no competition
22 between the two cations. Although the Ca concentrations used were lower
23 ($1.25 \times 10^{-3} M$), they used a much wider total Ca:total Zn ratio ($\approx 3300:1$).
24 Wide gaps between the sorption edges of alkaline earth cations and those
25 of transition metal cations have been reported (Kinniburgh et al., 1976;

1 Kinniburgh and Jackson, 1982). Under these assumptions, Kinniburgh and
 2 co-workers postulated that since adsorption is almost 100 % for the
 3 transition metals at pH values where alkaline earth cation sorption starts
 4 increasing, competition (exchange) will not be significant. From the data
 5 presented in Figures 1 and 3, it is suggested that the HFO-strips
 6 competitively sorb predicted amounts of dissolved Cu (Fig. 1a) and Zn
 7 (Fig. 1b) in a pH range of active Ca sorption (Fig. 3). Although at a pH
 8 > 9 there is significant Ca sorption (≈ 0.200 mol/mol Fe), it does not seem
 9 to interfere with transition metal adsorption. Concentrations of
 10 dissolved Cu and Zn at pH values of active Ca sorption were below
 11 detection limits, and amounts of metal sorption onto HFO-strips closely
 12 followed the ones predicted from dissolution of metal hydroxides (Fig. 2).

13 According to Dzombak and Morel (1990) selectivity in cation sorption
 14 onto oxides correlates fairly well with their first hydrolysis constant.
 15 Although deviations have been reported (e.g., see compilations in
 16 Fuerstenau et al., 1981 and Kinniburgh and Jackson, 1981), Schindler et
 17 al. (1976) suggest that the ligand properties of surface OH are basically
 18 not changed by the attached metal (e.g., Si, Fe, Al, Mn). Therefore,
 19 similar chemical bonding mechanisms between surface complexation of a
 20 cation and its hydrolysis are expected (Dzombak and Morel, 1990).
 21 Furthermore, according to Schindler (1981):





hydrolysis plus adsorption (Eq. [1] + Eq. [2]) is indistinguishable from surface complex formation (Eq. [3]).

Figure 4 shows adsorption of copper as a function of equilibrium concentration. Since sorption of transition metals onto the HFO-strips is very sensitive to changes in pH, small differences in the slopes of the pH edges (Fig. 1) will result in considerable differences in sorption isotherms between experimental and predicted values. Accordingly, MINTEQA2 predicted sorption at $pH\ 5.44 \pm 0.33$ (see Fig. 1a and 4a) more closely than at $pH\ 4.64 \pm 0.06$ (Fig. 1a and 4b). Similar results were obtained with Zn and Ni (Fig. 4b and 4c).

CONCLUSION

The modified HFO-strip technique, as previously reported for oxyanion sorption studies (Buselli and Amacher, 1994), proved to be a simple, reproducible method also for the quantitative removal of transition metal cations from solution. Recoveries of Cu, Zn, and Ni were greater than 96 %, as calculated by mass balance, in experiments where no precipitation products occurred.

This technique, unlike current methodology for the study of sorption at solid-liquid interfaces, allows determination and describes the behavior of metal cation sorption onto oxides at pH values higher than those required for metal hydroxide precipitation in the bulk solution. We

1 believe that the use of a easily removable solid phase, in conjunction
2 with spectroscopic techniques, could contribute significantly in our
3 understanding of sorption processes (adsorption/surface precipitation) at
4 oxide surfaces.

5 Under the conditions of the present study, surface coordination
6 (adsorption) seems to be the dominant sorption mechanism even at pH values
7 where considerable metal hydroxide precipitation occurs. Metal recovery
8 calculated from two *independent* measurements (dissolved and adsorbed)
9 closely followed the fraction of dissolved metal predicted by hydroxide
10 solubility constants. The relative order of transition metal sorption
11 onto the HFO-strips was: $\text{Cu} > \text{Zn} > \text{Ni}$, which agrees with sorption onto a
12 variety of pure and mixed sorbents present in soils and other natural
13 aqueous systems.

14 The modified HFO-impregnated filter paper technique is suitable for
15 the determination of multielement release from soils and other natural
16 aqueous systems. Although pH affects its uptake of ions from solution,
17 removal of both oxyanions (Buselli and Amacher, 1991) and transition metal
18 cations occurs in a wide range of pH.

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Table 1. Hydrous ferric oxide (HFO) parameters needed to model surface complexation using the diffuse-layer model.

Concentration of HFO (g/L of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) [†]	(g of Fe/L)*89/55.85
Type 1 sites (high-affinity) [‡]	0.010 moles/mole Fe
Type 2 sites (low-affinity) [‡]	0.400 moles/mole Fe
Specific Surface Area [§]	600 m ² /g

[†] Experimentally determined for each individual study

[‡] Experimentally measured from adsorption maxima - fixed for all studies

[§] from Dzombak and Morel (1990)

Table 2. Values of intrinsic constants used to model Cu/, Zn/ and Ni/HFO sorption with MINTEQA2 and the generalized two-layer model (FEO-DLM.DBS).

Surface Reactions		$\log K^{\text{int}}$	Source
<i>Protonation and Dissociation</i>			
$\equiv\text{FeOH}^\circ + \text{H}^+$	$\rightleftharpoons \equiv\text{FeOH}_2^+$	7.29	Dzombak & Morel (1990)
$\equiv\text{FeOH}^\circ$	$\rightleftharpoons \equiv\text{FeO}^- + \text{H}^+$	-8.93	Dzombak & Morel (1990)
<i>Metal Surface Complexation†</i>			
$\equiv\text{Fe}^{\text{S}}\text{OH}^\circ + \text{Ca}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{OHCa}^{2+}$	4.97	Dzombak & Morel (1990)
$\equiv\text{Fe}^{\text{W}}\text{OH}^\circ + \text{Ca}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OCa}^+ + \text{H}^+$	-5.85	Dzombak & Morel (1990)
$\equiv\text{Fe}^{\text{S}}\text{OH}^\circ + \text{Cu}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{OCu}^+ + \text{H}^+$	2.85	Dzombak (1986)
$\equiv\text{Fe}^{\text{W}}\text{OH}^\circ + \text{Cu}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OCu}^+ + \text{H}^+$	0.60	Dzombak & Morel (1990)
$\equiv\text{Fe}^{\text{S}}\text{OH}^\circ + \text{Zn}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{OZn}^+ + \text{H}^+$	0.97	Dzombak (1986)
$\equiv\text{Fe}^{\text{W}}\text{OH}^\circ + \text{Zn}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{OZn}^+ + \text{H}^+$	-1.99	Dzombak & Morel (1990)
$\equiv\text{Fe}^{\text{S}}\text{OH}^\circ + \text{Ni}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{S}}\text{ONi}^+ + \text{H}^+$	0.15	Dzombak (1986)
$\equiv\text{Fe}^{\text{W}}\text{OH}^\circ + \text{Ni}^{2+}$	$\rightleftharpoons \equiv\text{Fe}^{\text{W}}\text{ONi}^+ + \text{H}^+$	-2.50	Dzombak & Morel (1990)

† Superscripts refer to high-affinity "strong" sites (S) and low-affinity "weak" sites (W), see Dzombak

Table 3. Solubility products for metal hydroxides used by the thermodynamic database attached to MINTEQA2.

Dissolution Reactions			$\log {}^*K_{so}^\dagger$
$Cu(OH)_2(s) + 2H^+$	\rightleftharpoons	$Cu^{2+} + 2H_2O$	8.64
$Zn(OH)_2(s) + 2H^+$	\rightleftharpoons	$Zn^{2+} + 2H_2O$	12.45
$Ni(OH)_2(s) + 2H^+$	\rightleftharpoons	$Ni^{2+} + 2H_2O$	10.80

$^\dagger \quad \log K_{so} = (\log {}^*K_{so}) + (z \cdot \log K_w)$, for the reactions above, $z = 2$ (see Sposito, 1981, p. 67). ${}^*K_{so}$ data from Baes & Mesmer (1976).

Table 4. Recovery of metal cations using the modified HFO-impregnated filter paper technique. Adsorption of cations as a function of equilibrium solution concentration, initial concentrations ranging from 10^{-6} to 10^{-3} M.

Metal	Recovery (%) [†]	n	SE	C.V. (%)
Copper	97.8	72	0.7	6.4
Zinc	96.7	24	0.7	3.8
Nickel	97.8	24	0.5	2.6

[†] [(moles sorbed by HFO-strip + moles in solution)/(initial moles)]*100

FIGURES

Figure 1. Adsorption envelopes for Cu, Zn, and Ni. Solid squares (■): metal removed by HFO-strips; hollow squares (□): sorption calculated from final dissolved metal concentration; dotted line (...): adsorption predicted by MINTEQA2/FEO-DLM.DBS.

Figure 2. Percent metal in solution as a function of pH. Dotted line (...): percent dissolved metal cation predicted by MINTEQA2 with no adsorbent present; hollow circles (○): experimental % dissolved metal in solution, HFO-strip present. Experimental recoveries (metals adsorbed by HFO-strip + dissolved metal in solution) are represented by solid circles (●).

Figure 3. Adsorption envelopes for calcium. Experimental conditions are those shown in Figure 1. Symbols represent experimental data and lines are MINTEQA2/DLM predictions.

Figure 4. Adsorption isotherms for: (a) copper at 5.44 ± 0.33 and (b) at 4.64 ± 0.06 , (c) zinc at pH 6.41 ± 0.14 , and (d) nickel at pH 6.49 ± 0.12 . Model predictions were calculated for each total concentration and solution equilibrium pH.

Figure 1

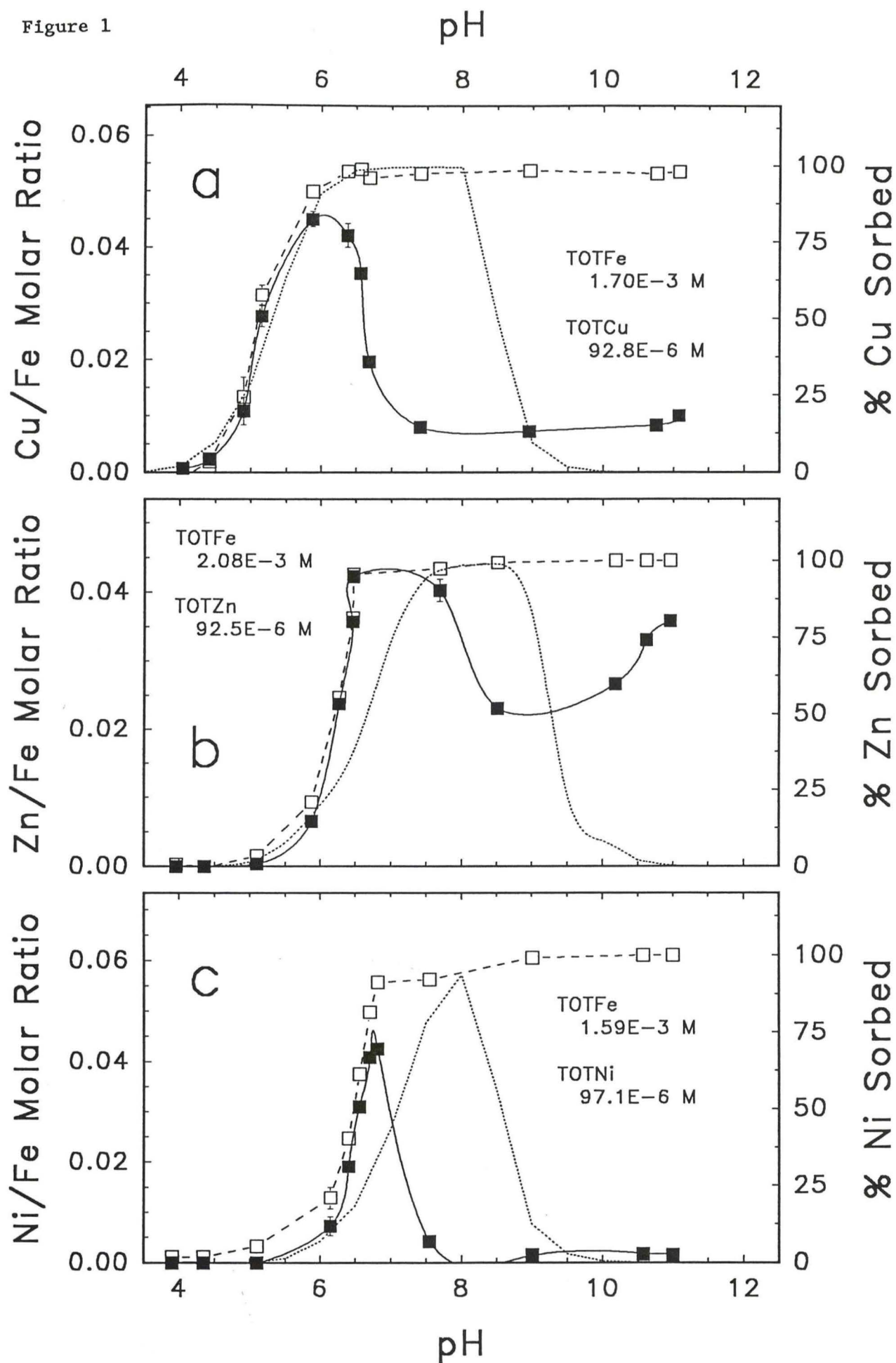
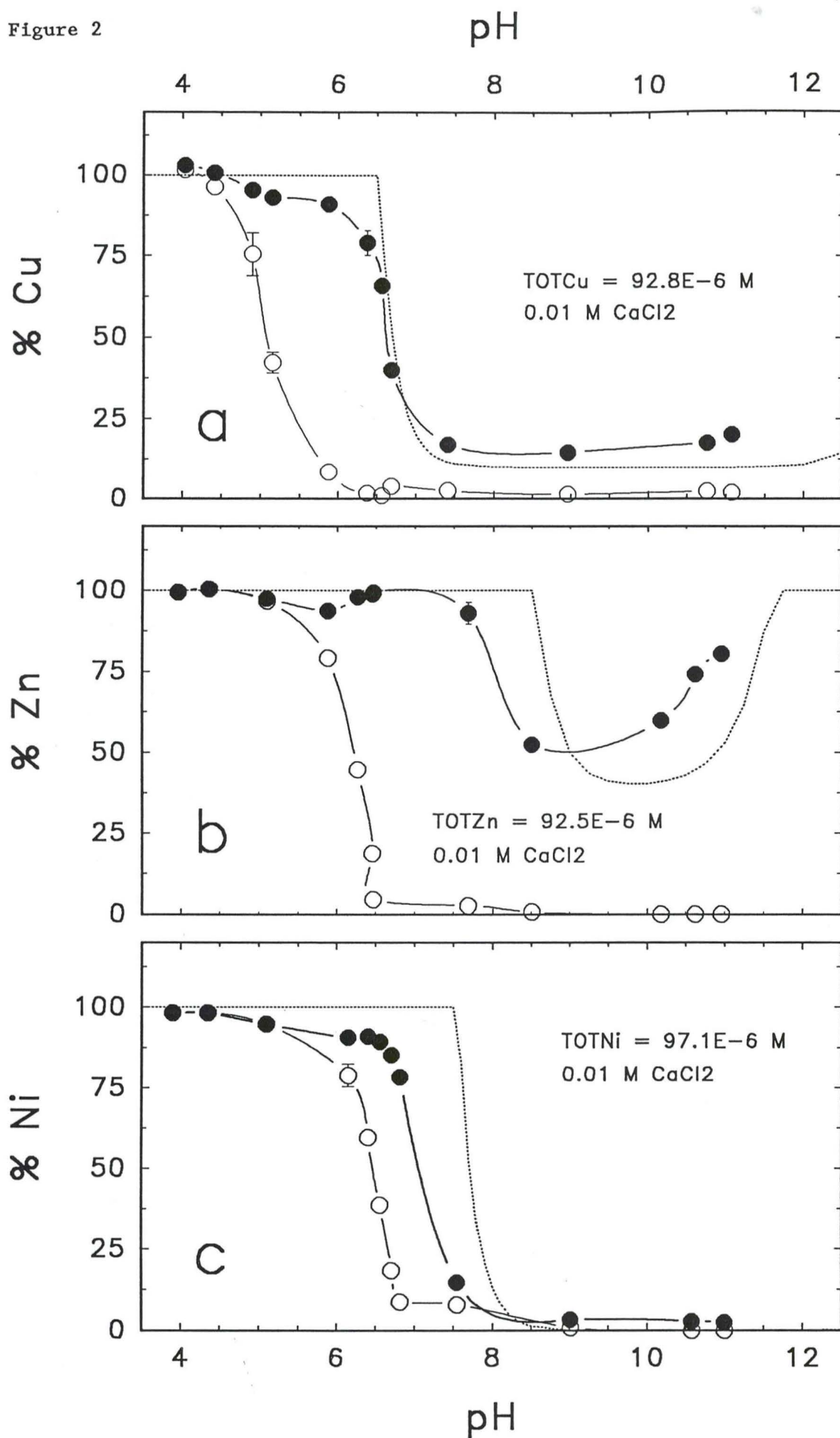


Figure 2



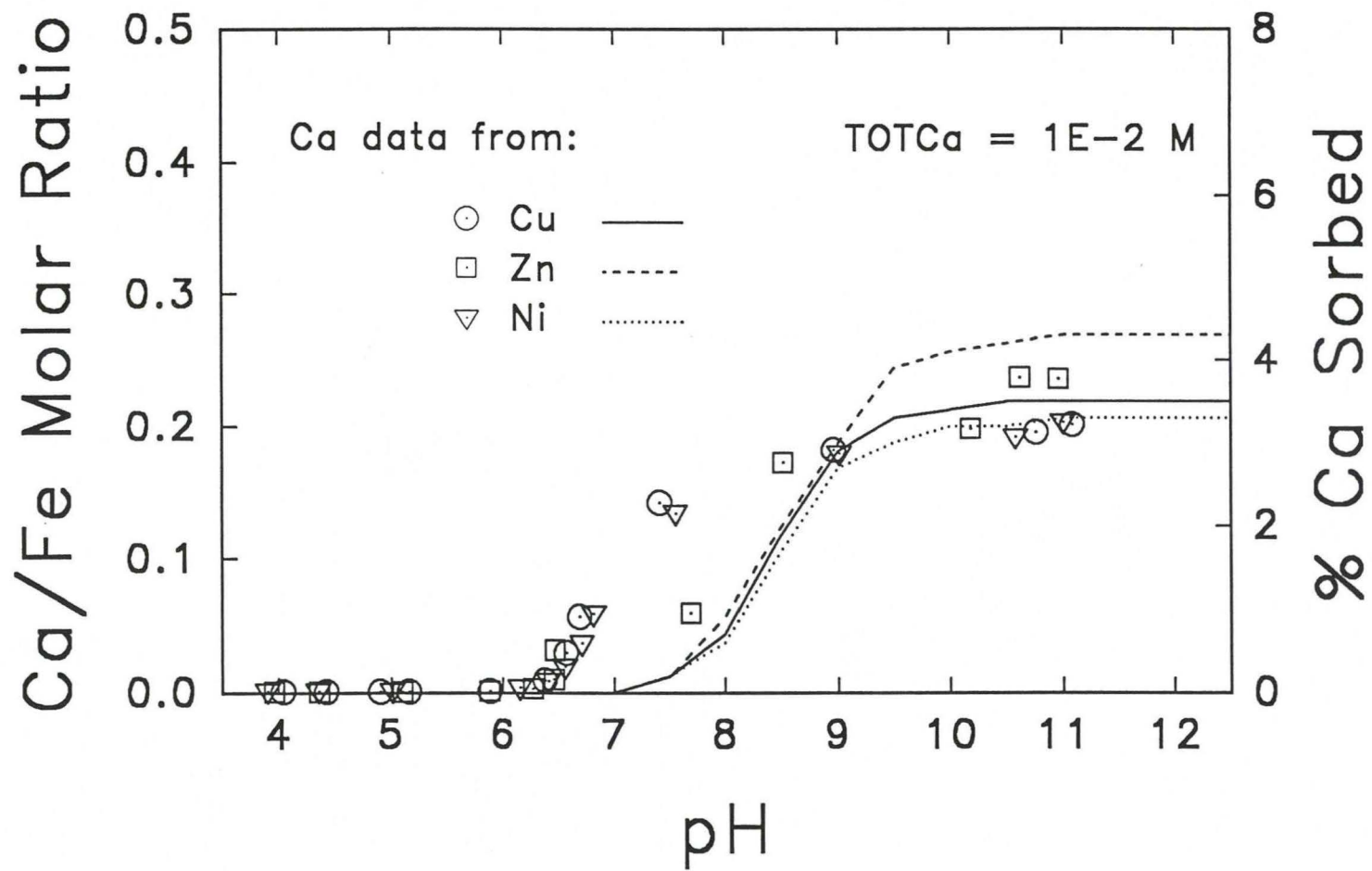


Figure 3

Figure 4

